BIOMASS AND BIOENERGY 49 (2013) 86–94

Available online at www.sciencedirect.com

SciVerse ScienceDirect

http://www.elsevier.com/locate/biombioe

Hydrothermal carbonization: Fate of inorganics

M. Toufiq Reza, Joan G. Lynam, M. Helal Uddin, Charles J. Coronella*

Department of Chemical & Materials Engineering, University of Nevada, 1664 N. Virginia St., MS 0170, Reno, NV 89557, USA

ARTICLE INFO

Article history:
Received 20 October 2012
Received in revised form
1 December 2012
Accepted 5 December 2012
Available online 12 January 2013

Keywords:
Inorganic elements
Heavy metals
Fouling index
Lignocellulosic biomass
Hydrochar
Biomass pretreatment

ABSTRACT

Hydrothermal carbonization (HTC) is a pretreatment process for making a homogenized, carbon rich, and energy-dense solid fuel, called biochar, from lignocellulosic biomass. Corn stover, miscanthus, switch grass, and rice hulls were treated with hot compressed water at 200, 230, and 260 °C for 5 min. Mass yield is as low as 41% of the raw biomass, and decreases with increasing HTC temperature. Higher heating values (HHV) increase up to 55% with HTC pretreatment temperature. Up to 90% of calcium, magnesium, sulfur, phosphorus, and potassium were removed with HTC treatment possibly due to hemicellulose removal. At a HTC temperature of 260 °C, some structural Si was removed. All heavy metals were reduced by HTC treatment. The slagging and fouling indices are reduced with HTC treatment relative to that of untreated biomass. Chlorine content, a concern only for raw and HTC 200 switch grass, was reduced to a low slagging range at 230 °C, and 260 °C. Alkali index was medium for raw biomass but decreased by HTC.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The world is facing two vital challenges in current energy demand: energy supply and sustainability. Limited fossil fuel reserves and their environmental impact intensifies interest in the use of biomass, one of the largest energy resources. Biomass is an alternative, renewable, and sustainable energy source with a large potential to mitigate the energy crisis. About 450 million dry tons of wood, energy crops, and agricultural residues both primary and secondary are available currently in the US and the amount is expected to increase to more than 1000 Mt by 2030 [1]. Feedstock supply and logistics of lignocellulosic biomass, such as wood, rice hulls, straw, and switch grass, are challenging due to low bulk density, low energy density, and high ash content [2–4]. Hydrophilic biomass is subjected to biological deterioration, limiting the practical time for storage, a challenge for seasonally available agricultural residues. A pre-treatment process which can overcome these limitations of biomass usage for energy is essential.

Hydrothermal carbonization (HTC) is a prominent pretreatment process for biomass enhancement [5–7]. In HTC, biomass is treated with hot compressed water resulting in three products: gases, aqueous chemicals, and a solid product known as HTC biochar. Reaction temperatures are in the range of 200–275 °C, and the pressures are maintained above the saturation pressure to ensure the liquid state of water. The gas product is about 10% of the original biomass, consisting mainly of CO_2, while the aqueous extractive compounds are primarily sugars, acetic acid, and other organic acids [9,30]. The solid product contains about 41–90% of the mass and 80–95% of the fuel value of the original feedstock [8–10]. HTC processes make a solid char with higher energy density that is easily friable and more hydrophobic than the original biomass [11]. The reaction mechanisms are still poorly understood [9,12].

---

* *Corresponding author*. Tel.: +1 775 784 4253.
E-mail address: coronella@unr.edu (C.J. Coronella).

0961-9534/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biombioe.2012.12.004

Plants acquire inorganics, which are necessary for their metabolic pathways, from the soil in which they are grown. Inorganics are in the form of inorganic salts, bound to the organic structure by ionic bonds, or possible covalent bonds in a cross-linked matrix [17]. Woody biomass contains less inorganic content than grasses or agricultural residues [13,14]. Due to their high melting point, the inorganics usually remain in the ash, which usually has a negative impact on biomass firing or even co-firing with coal [15]. During combustion, ash must be removed from the boiler, as it increases the complexity in co-firing as well as lowers the efficiency of boiler. Moreover, sodium, potassium, calcium, and other metals can cause slagging and fouling, resulting in lower power plant efficiency [16,17]. Alkali metals react with silica to form alkali silicates, which soften below 700 °C and thus cause undesirable slagging. They also react with sulfur to make alkali sulfate, which deposits on heat transfer surfaces, reducing the efficiency of the combustion process [18]. Chloride, which is very corrosive for stainless steel, can also react with alkalis and silicates to form an undesirable stable slag [14]. Heavy metals like mercury, lead, arsenic, chromium, copper, zinc, and selenium are scarce in biomass [12]. However, they are concentrated by about an order of magnitude in ash. For these reasons, elimination or at least reduction of inorganic components including heavy metals is important in promoting biomass combustion.

Based on different mechanisms involved in ash deposit on the heat transfer surface, two general types of ash deposition have been defined as slagging and fouling [18]. Slagging is the formation of molten or partially fused deposits on furnace walls or convection surfaces exposed to radiant heat. Fouling is defined as the formation of deposits on convection surfaces such as superheater and reheaters [17]. The viscosity of the coal ash slag determines the affects on its erosivity, and the diffusivity of ions within the slag which affects its corrosivity [35].

Slagging and fouling tendencies in coal combustion have been well studied for years. Different correlations have been suggested based on the ash composition of coal. Slagging index, fouling index, alkali index, ratio-slag viscosity index, and chlorine content are the common indices for coal [19]. The ash compounds may be separated into two groups based on their melting point. The first group has lower melting temperatures and typically contains Fe_2O_3, CaO, MgO, Na_2O, or K_2O. The other group of higher melting temperature compounds includes SiO_2, Al_2O_3, and TiO_2. Phosphorus sometimes is added into the former group, since P_2O_5 has a relatively high melting point. The slagging index is the measure of scale produced from those two groups in presence of sulfur, while the fouling index is almost identical but includes the sodium and potassium oxides influence. The alkali index is the amount of sodium and potassium oxides present per GJ of solid fuel. The slag viscosity index is the percentage of silica present in the metal oxides. Several indices, along with ratings, are defined in Table 1.

The main goal of this work is to characterize HTC biochar of grassy biomass and agricultural residues. Inorganic analysis of HTC biochar is reported and describes quantitatively. Heavy and trace metal leaching has been examined. Probable slagging and fouling behavior of untreated and HTC treated biomass have been determined by calculation of several indices, using elemental analysis of ash.

2. Material and methods

2.1. *Material*

Four types of lignocellulosic biomass were evaluated by HTC in this study. Corn stover and miscanthus were provided by Idaho National Laboratory. Corn stover was harvested in Emmetsburg, Iowa during October, 2011. Miscanthus was harvested in Urbana, Illinois during September 2011. Rice hull was harvested in Gridley, California during September 2008, and switch grass was harvested in Fallon, Nevada in October 2007. Corn stover, miscanthus, and switch grass were comminuted to 18 mm by Bliss hammer mill model 4460 (Ponca City, OK). Harvested biomass were dried in a warehouse by free air circulation for a month and stored in plastic container in a dry storage until further use. To promote a more homogeneous biomass reactant and provide effective sub-

Table 1 – Slagging, fouling, alkali, and ratio-slag indices, Cl content, definition and their limits [14].

Slagging/fouling index	Expression	Limit
Slagging index	$I_s = (B/A)*S^d$ S^d = % of S in dry fuel	$I_s < 0.6$ low slagging inclination $I_s = 0.6 - 2.0$ medium $I_s = 2.0 - 2.6$ high $I_s > 2.6$ extremely high
Fouling index	$I_F = (B/A)*(Na_2O + K_2O)$	$I_F \le 0.6$ low fouling inclination $0.6 < I_F < 40$ medium $I_F \ge 40$ high
Alkali index	$I_A = (Na_2O + K_2O)$ in kg/GJ	$0.17 < I_A < 0.34$ slagging/fouling probable $I_A \ge 0.34$ slagging/fouling is certain
Slag viscosity index	$I_V = (SiO_2*100)/(SiO_2 + MgO + CaO + Fe_2O_3)$	$I_V > 72$ low slagging inclination $65 \le I_V \le 72$ moderate $I_V < 65$ high
Chlorine content	Cl as received (%)	Cl < 0.2–0.3 low slagging inclination 0.2 < Cl < 0.3 medium 0.3 < Cl < 0.5 high Cl > 0.5 extremely high

critical water diffusion in the biomass, a blender was used to reduce the raw biomass size. Samples were sieved to −1.18 mm + 0.60 mm, air dried, and stored in a sealed ziplock bag until treatment.

2.2. Hydrothermal carbonization

Hydrothermal carbonization of biomass was performed in a 100 cm^3 Parr bench-top reactor (Moline, IL) at three temperatures 200, 230, and 260 °C. The temperature of the reactor was controlled using a PID controller. The reactor pressure was not controlled but indicated by the pressure gauge and ranged from 1 to 5 MPa. For each run, a mixture of biomass and water with a ratio of 1:5 (weight basis), was loaded into the reactor. Nitrogen was passed through the reactor at the rate of 80 cm^3 min^{-1} for 10 min to purge oxygen. The reactor was heated to the desired temperature and maintained at that temperature for 5 min. The reactor then was cooled rapidly by immersion in an ice-water bath until it reached room temperature. The gas produced was released to the atmosphere. The condensed products were filtered by Whatman 40 filter paper and the solid was put in a drying oven at 105 °C for 24 h before further analysis. HTC 200, HTC 230, and HTC 260 are the names given to solid biochar products of HTC at temperatures 200 °C, 230 °C, and 260 °C, respectively.

2.3. Analyses

2.3.1. Induced coupled plasma – atomic emission spectrophotometry (ICP-AES)

A Varian Vista Pro ICP-AES was used for inorganic analysis. Acid digestion was used to dissolve solid sample for ICP-AES. A volume of 5 cm^3 of 99.5% pure HNO_3 was added to 0.4 g of dry solid sample. A volume of 0.5 cm^3 of 50% volume basis hydrofluoric acid (HF) was added to the solution to dissolve the SiO_2. Liquid argon at the rate of 88 cm^3 min^{-1} was used as carrier to ICP process. The liquid solution was heated to 80 °C and maintained at that temperature for 4 h. After 4 h, the sample was removed from the oven and cooled for 5 h. To prevent HF from reacting with the torch, 0.5 g solid Boric Acid (98% pure) was put into the solution, so that unused HF would react with $B(OH)_3$ to form fluroboric acid (HBF_4), which is invisible and not harmful for ICP-AES [36]. The reaction can be occur in the room temperature and fluroboric acid behaves inert for ICP-AES. The solution was diluted 20–200 times before injection into the ICP-AES machine, with 5% ethanol-water used as the solvent.

2.3.2. Higher heating value

The higher heating values (HHV) for the untreated biomass and the biochar products were measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) fitted with continuous temperature recording. All samples (0.5 g each) were dried at 105 °C for 24 h prior to analysis, and HHV are reported on a dry, ash free basis.

2.3.3. Ash measurement

ASTM D 1102 method was followed for ash determination of HTC biochar. 0.5–2.0 g of dry sample was heated in the muffle furnace at 575 °C for 24 h. Each experiment was done three times for better precision. The ash was store in the ziplock bag for SEM analysis.

2.3.4. Fiber analysis

The van Soest method of NDF-ADF-ADL (neutral detergent fiber, acid detergent fiber, acid detergent liquid) dissolution was used to determine the percentage of hemicellulose, cellulose and lignin in solid samples [20]. The contents of hemicellulose, cellulose, lignin, and extractives were calculated from the difference of NDF, ADF, ADL, and ash. Sample mass that is not assigned to one of those fractions consists of aqueous soluble polysaccharides, saccharides, proteins, starch, or other components. According to van Soest method the solid residue left after NDF, ADF, and ADL is lignin and ash. Ash, determined separately by muffle furnace, subtracted from lignin and ash weight from fiber analysis, to find lignin content. So, lignin is not measured directly and this is one of the main shortcoming of this method. Biomass is divided into five components only in this method and any change of one component will affect the others. Samples were dried at 105 °C for 24 h prior to fiber analysis.

2.3.5. Scanning Electron Microscopy (SEM)

A FE-SEM Hitachi Scanning Electron Microscope (SEM) model S-4700 was used for visualization. Ash samples of raw biomass, HTC-200, HTC-230, and HTC-260 biochar were analyzed in the SEM. The samples were maintained on special studs and platinum coated with polaran coater tar 5000, under an argon atmosphere for a coating thickness of approximately 1000 Å. The samples were dried in a 105 °C oven for 24 h prior to analysis. An energy dispersive X-ray (EDX) detector was used to determine the semi-quantitative inorganic analysis of ash samples. For the EDX detector, the sample distance from the lens was maintained at 11.8 mm and an area of 250 μm × 200 μm was analyzed for elemental detection. The average of five different sites was taken to increase the accuracy.

3. Results and discussion

3.1. Fiber analysis of HTC biochar

Table 2 shows fiber analysis results for HTC biochars along with their raw biomass sources. Raw corn stover has 26.3% extractives, which is very high compared to miscanthus, rice hulls, or switch grass, which have 6.9%, 12.9%, and 13.6% extractives, respectively. Monomeric sugars (mainly glucose and fructose) along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides are the main components of extractives in grassy biomass [21]. Hemicellulose is a heteropolymer composed of sugar monomers, including xylose, mannose, glucose, and galactose with β-(1-4) glucosidic bonds [5,22]. Rice hulls had only 14.9% hemicellulose, compared to the other three feedstocks which had 26–33% hemicellulose. Cellulose, a polysaccharide of glucose with β-(1-4) glucosidic bonds, was found to be 30–44% of the four raw biomass, with miscanthus at the higher end. The four raw biomass studied had 9–15% lignin, which is a high molecular weight cross-linked polymer of phenyl propane

Table 2 – Fiber analysis, ash yield and HHV of various biomass and their HTC biochar.

Biomass	Condition	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Extractives (%)	Ash (%)	Mass yield (%)	Ash yield (%)	HHV (MJ/Kg)
Corn Stover	Raw	26.3	29.7	9.5	26.3	8.2	100	100	15.6
	HTC 200	0.0	51.1	8.2	32.4	8.3	82	83.0	19.1
	HTC 230	0.0	48.0	9.9	33.6	8.9	57	61.9	20.0
	HTC 260	0.0	8.6	27.4	56.0	8.1	41	40.5	24.1
Miscanthus	Raw	30.2	44.4	14.2	6.9	4.4	100	100	17.4
	HTC 200	2.1	49.5	16.1	28.1	4.1	79	73.6	20.6
	HTC 230	0.0	55.1	17.3	23.6	4.1	64	59.6	19.8
	HTC 260	0.0	21.0	39.7	35.4	4.1	57	53.1	22.0
Switch grass	Raw	33.7	35.3	8.4	13.6	9.1	100	100.0	15.3
	HTC 200	0.0	46.4	9.1	35.0	9.9	87	94.6	19.0
	HTC 230	0.0	38.4	17.4	35.3	9.4	67	69.2	19.7
	HTC 260	0.0	22.9	20.8	47.0	9.5	58	60.5	21.0
Rice hull	Raw	14.9	39.8	11.3	12.9	21.1	100	100	20.3
	HTC 200	0.0	42.4	12.6	23.0	25.0	85	100	20.3
	HTC 230	0.0	37.9	13.3	25.0	26.0	77	94.9	20.9
	HTC 260	0.0	23.0	20.0	29.4	29.8	54	76.3	24.6

derivatives [17]. Miscanthus had high lignin relative to other biomass feedstocks at 15% lignin. However, its lignin content was still lower than that of woody biomass, which contains 25–30% lignin [10].

In hydrothermal carbonization, subcritical water is used because its ionic constant is increased nearly two orders of magnitudes and liquid water behaves as a non-polar solvent at temperatures of 200–280 °C [23]. Water (liquid) at 200 °C breaks the β-(1-4) glycosidic bonds of hemicellulose [5], degrades into sugar monomers, which further degrade into furfurals and other compounds, including 5-HMF (hydroxyl methyl furfural) [24]. There is no evidence of hemicellulose remaining in any of the HTC biochar products, as shown in Table 2. Cellulose, on the other hand, requires more severe conditions to break its β-(1-4) glycosidic bonds [5]. Cellulose can degrade into oligomers, a portion of which hydrolyzes into glucose with the remainder forming a cross-linked polymer [25]. HTC 200 biochar shows an increase in cellulose percentage relative to raw biomass, probably due to elimination of hemicellulose. HTC 230 and HTC 260 biochars show a decreasing trend in cellulose content for every biomass studied, but cellulose still remains in the HTC biochar product in each case. At temperatures between 200 and 260 °C, water barely degrades lignin and produces a small amount of oligomers, oils and gases [5,29]. Table 2 shows an increase in lignin percentage in the HTC biochar with reaction temperature, as hemicellulose and cellulose are degrading. Cross-linked polymer produced from cellulose degradation may have solubility characteristics similar to lignin [7], and would be characterized as lignin using this fiber analysis technique. Reza et al., reported that at a 260 °C reaction temperature, loblolly pine biochar's lignin percentage increases to about 3 times that of the raw pine [28]. Moreover, the degradation of hemicellulose, cellulose, and extractives leaves a porous HTC biochar solid product with concentrated sugars and organic acids dissolved in water. The porous structures often absorb dissolved sugars and furfurals during HTC so that extractives percentage increases in the HTC biochar [6]. The concentration of 5-HMF in the liquid product increases quite significantly with increasing HTC temperature [26,30]. HTC 260 corn stover has 56% extractives and HTC 260 switch grass has 47% extractives, somewhat higher than other two HTC 260 biochars. These results suggest that HTC biochar of grassy biomass may produce a more porous biochar structure than woody biomass or other agricultural residues [7,27].

3.2. *Mass yield and energy value of HTC biochar*

A series of HTC experiments were conducted on four different biomass, each with distinctive monomer building blocks of hemicellulose, lignin, and extractives. Mass yield (the ratio of solid biochar product to the original raw biomass from which it was produced) and higher heating value (HHV) are two very important characteristics of HTC biochar, and are reported in Table 2. Mass yield decreases for all biomass types with increasing HTC reaction temperature, while HHV increases with HTC temperatures [8,10]. Hemicellulose degrades completely at reaction temperatures of 200 °C or higher, but mass yield is higher than would be expected considering this loss likely due to the deposition of dissolved compounds, as discussed earlier. For corn stover, the HTC mass yields are lower than yields of any other biomass studied. The low cellulose content and high extractives content of corn stover may be the reason for such a low mass yield.

Table 2 shows the higher heating values (HHV) of the four biomass investigated along with the values for their HTC biochar. In general, the HHV of biomass components follow this trend: ash < extractives < hemicellulose < cellulose < lignin, reflecting the trend of increasing carbon content [7]. However, the HHV of extractives depend on their composition [12]. It has been previously reported [12] that carbon content of HTC biochar increases with HTC temperature, so the result shown here of increasing HHV with reaction temperature is expected. Reflecting the decomposition and removal of hemicelluloses and extractives (both relatively highly oxygenated with low fuel value) HTC 260 biochar produced from corn stover has HHV 54% higher than the original feedstock. Under the same conditions, switch grass, miscanthus, and rice hulls exhibit 37%, 26%, and 21% increases in HHV, respectively. HHV increases in rice hulls as well but it is below that observed in other biomass at all temperatures. Rice hulls have low content of reactive fractions (extractives and hemicellulose), which explains the relatively low increase in HHV. In contrast, corn stover, switch grass, and miscanthus show an increase of 18–22% in the HHV even at 200 °C, compared to the raw biomass. These three biomass have higher extractives and hemicellulose (but lower ash) compared to rice hulls. Removal of these two relative components results in an increase of the C:O ratio, which ultimately increases the energy value. Moreover, hemicellulose and cellulose degrade into monomers, furfurals, and 5-HMF under subcritical water conditions. The higher HHV of 5-HMF (22.06 MJ kg^{-1}) compared to hemicellulose (17.58 MJ kg^{-1}) and other extractives (glucose is 15.57 MJ kg^{-1}) may increase HHV if 5-HMF is deposited in the porous biochar structure [9,31,32]. Since 5-HMF is produced with the HTC process at higher reaction temperatures from the degradation of cellulose, it may augment HHV in HTC biochar [26,30]. This phenomena may explain the higher HHV of HTC biochar compared to dry torrefied biochar at the same temperature with even a longer reaction time [10].

3.3. *Ash yield of HTC biochar*

Every biomass has specific amounts and types of inorganics in its structure. In addition, extra inorganic material, such as loose dirt from harvesting, may cling to biomass. Loose minerals (dirt) collected during harvesting, can be removed by a mild hot water wash [21]. Furthermore, there is some expectation that additional acidity produced in HTC may solubilize and remove inorganics [9].

Table 2 shows the ash content and ash yield of HTC biochar for the four biomass studied. Ash yield can be defined as the ratio of percentage of HTC biochar ash with raw feedstock ash multiplied by the mass yield. Raw rice hulls contain 21% ash and ash content increases with increasing reaction temperature. HTC 260 rice hulls biochar has 29.8% ash, which is 41% higher than raw rice hulls. Raw corn stover, miscanthus, and switch grass have ash contents of 8.2%, 4.4%, and 9.1%, respectively, while HTC 260 biochar of these three have 8. 1%, 4.1%, and 9.5%, respectively. With the exception of rice hulls, the ash yield follows closely the mass yield; so, loss of biomass correlates with loss of inorganic ash.

Corn stover and miscanthus show a significant decrease (83%, and 74% respectively) in ash yield when treated at 200 °C. Conversely, switch grass and rice hull undergo a very little or no change (95% and 100%, respectively) when treated at 200 °C. One possible explanation for this behavior is that corn stover and miscanthus have more loose dirt accumulated during harvesting. Alternatively it is possible that a large part of structural inorganics exist in hemicellulose or extractives, which are removed with HTC. The ash yield with a HTC reaction temperature of 260 °C is significantly reduced for all four biomass. Cellulose starts reacting at 230 °C under hydrothermal conditions, causing the biochar to become porous [7]. This porosity may permit the inorganics previously entrapped or loosely bonded in a crosslinked matrix to leach out. Corn stover's reduction in ash yield with HTC is quite remarkable, but the other three biomass show significant decreases as well.

3.4. *Inorganic analysis of HTC biochar*

From the ash yield, it is clear that each biomass is leaching inorganics with increasing severity in hydrothermal reaction conditions. Fig. 1 shows the quantitative inorganic yield of

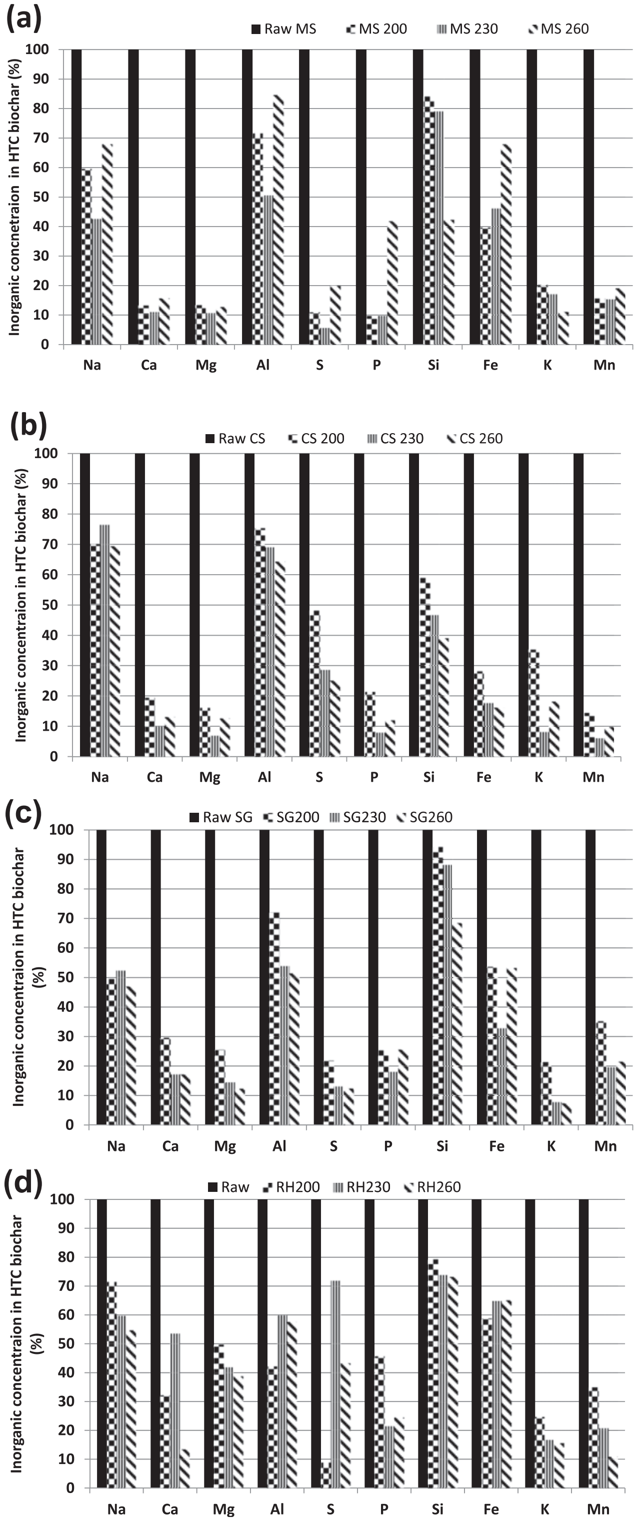

Fig. 1 – Inorganic elemental yield (ratio of individual inorganic element in HTC biochar with raw multiplied by mass yield) of raw and HTC biochar of various feedstocks (a) miscanthus, (b) corn stover, (c) switch grass, and (d) rice hull.

Table 3 – Inorganic concentration in one kg of raw biomass.

Raw biomass	Na (mg)	Ca (mg)	Mg (mg)	Al (mg)	S (mg)	P (mg)	Si (mg)	Fe (mg)	K (mg)	Mn (mg)
Miscanthus	1451	3722	1144	2019	776	661	11,400	137	2302	151
Corn Stover	2732	4955	2197	3114	1090	1172	15,388	1617	9808	103
Switch grass	2607	5841	2221	2800	989	1170	14,244	190	10,991	72
Rice hull	5360	292	314	4664	115	96	35,910	38	2563	73

HTC biochar using ICP-AES. Inorganic yield is the ratio of inorganic content of HTC biochar with raw feedstock multiplied by mass yield at a given temperature. The primary inorganic elements present in the raw biomass are presented with their concentration in Table 3. Silica is the main inorganic component found in the four biomass studied, although there are other inorganics, such as sodium, potassium, aluminum, sulfur, magnesium, and phosphorus, in smaller quantities, along with trace amounts of heavy metals. The silica content of raw miscanthus is 11.4 g kg^{-1}, while switch grass, corn stover, and rice hull have 14.5, 15.0, and 40 g kg^{-1} of raw biomass respectively, which is consistent with the literature [3,14,15,33,34]. It can be seen in Fig. 1 that HTC removes little Si. Si is very stable in a $SiO_2 \cdot nH_2O$ form in rice hulls or is covalently bonded within biomass' organic matrix [17,33]. The decrease in Si yield with HTC at 200 °C may be the result of loose dirt removal. At 260 °C, where lignin likely starts reacting, some silica is removed. This effect is visible for every biomass except rice hull, where the Si concentration at 260 °C is similar to that at other reaction temperatures.

MostCa, S, P, Mg, and K in lignocellulosic biomass exists in either the hemicellulose or extractives [18]. Of these inorganics, 50–90% can be removed by hot water leaching [17]. Hydrothermal carbonization at 200 °C can be very effective in removing these inorganics, as shown in Fig. 1. The percentages removed of these inorganics are 65–83% for corn stover, 75–90% for miscanthus, 70–79% for switch grass, and 50–90% for rice hull. For phosphorus, 75–90% is removed at 200 °C for miscanthus, corn stover, and switch grass, but only 54% is removed with rice hulls. When HTC temperature is increased to 230 °C, additional Ca, Mg, K, S and P are removed from miscanthus, corn stover, and switch grass, but rice hull only shows reduced P and K. At 260 °C, all the hemicelluloses and extractives have been reacted and much of the cellulose has reacted as well, leaving behind a porous solid. Porous structure might absorb some inorganics, which might explain the increase of Ca, P, Mg, and K from HTC 230 to HTC 260 is found: 48–76% for corn stover.

3.5. *Heavy metal analysis of HTC biochar*

Heavy metals like Hg, Pb, Cd, Cr, Cu, Zn, As, Ni, Ag, and Se exist in trace amounts in biomass. Nevertheless, in using HTC biochar and its ash, data about heavy metal content is essential due to environmental issues. Table 4 shows the heavy metal content in HTC biochar. Hg and Se concentrations are below the detection limit of ICP-AES. Heavy metals are found in this range: 1–20 mg Ni, 5–17 mg Ag, 27–34 mg Pb, 6–45 mg Zn, 3–14 mg Cu, 1–44 mg As, 9–52 mg Cd, and 2–14 mg Cr per kg of raw biomass. Only Cd for all raw biomass and As for raw rice hull exceeds the soil protection act limit [12]. These heavy metals have high melting points and as a result they are concentrated in the ash after combustion, sometimes by an order of magnitude. There could be compliance issues in disposal of raw biomass ash. Low temperature HTC treatment is effective for heavy metal reducing. All the heavy metals except Pb and As are found in concentrations less than 15 mg per kg of HTC 200 for every biomass. Pb and As are relatively inert to HTC reactions.

Table 4 – Heavy metal concentration in one kg of biomass and HTC biochar.

Biomass	Condition	Ni (mg)	Ag (mg)	Pb (mg)	Zn (mg)	Cu (mg)	As (mg)	Cd (mg)	Cr (mg)
Corn Stover	Raw	20.3	14.1	26.6	45.3	13.8	44.4	9.0	14.0
	HTC 200	4.5	4.0	24.9	14.7	8.4	35.2	2.2	6.3
	HTC 230	5.1	2.7	12.3	12.6	9.1	25.9	1.1	5.4
	HTC 260	5.6	1.8	20.2	18.7	10.6	26.3	1.1	5.8
Miscanthus	Raw	12.6	10.4	29.3	35.1	4.0	7.3	30.2	6.8
	HTC 200	2.1	2.8	29.4	5.2	0.7	0.7	25.8	0.8
	HTC 230	3.1	3.1	35.1	8.8	3.3	0.5	29.9	0.7
	HTC 260	5.8	2.4	24.2	10.3	7.9	6.0	22.7	1.2
Switch grass	Raw	14.8	16.8	30.4	37.0	8.3	11.4	51.9	11.0
	HTC 200	3.8	2.3	34.9	8.3	10.0	0.8	30.4	0.9
	HTC 230	2.3	2.0	24.0	4.6	4.2	1.2	31.5	1.0
	HTC 260	9.2	2.1	30.8	11.7	15.4	8.4	18.2	1.2
Rice hull	Raw	1.3	4.8	34.4	5.9	3.1	1.2	16.2	1.9
	HTC 200	3.2	2.8	34.2	4.6	3.0	1.3	14.2	1.5
	HTC 230	2.9	2.4	35.4	4.1	1.8	1.6	18.9	0.7
	HTC 260	2.7	2.2	34.7	5.4	5.9	1.5	2.8	1.7

Table 5 – Elemental metal analysis of HTC biochar ash by SEM-EDX.

Biomass	Condition	Na (%)	Ca (%)	Mg (%)	Al (%)	S (%)	P (%)	Si (%)	Fe (%)	K (%)	Cl (%)
Corn Stover	Raw	0.5	10.3	3.9	4.2	0.9	1.8	38.3	3.1	34.9	2.1
	HTC 200	0.9	9.1	2.4	4.3	3.5	2.5	46.9	3.9	25.3	1.4
	HTC 230	0.9	8.1	1.8	6.1	3.1	3.3	57.9	4.4	14.0	0.5
	HTC 260	0.7	7.4	2.0	6.5	3.0	1.6	56.8	4.5	17.2	0.3
Miscanthus	Raw	0.7	14.7	3.7	0.6	0.9	2.7	64.2	0.6	10.6	0.2
	HTC 200	0.8	13.3	2.8	0.7	2.2	4.7	64.2	1.1	9.3	0.3
	HTC 230	Trace	11.1	1.4	0.6	2.9	3.9	75.9	1.5	4.3	0.1
	HTC 260	Trace	7.9	1.9	0.7	2.5	2.4	74.5	1.7	5.3	Trace
Switch grass	Raw	1.0	12.4	5.0	0.3	0.7	3.0	47.8	0.4	24.5	4.6
	HTC 200	0.9	11.0	3.2	0.4	1.5	3.9	50.8	0.6	23.8	6.0
	HTC 230	Trace	11.5	1.3	0.5	1.2	3.7	70.9	1.0	9.1	1.0
	HTC 260	Trace	10.9	1.0	0.4	0.9	4.8	71.8	0.9	6.7	1.0
Rice hulls	Raw	0.3	2.3	0.6	0.1	0.6	0.4	85.3	0.2	9.2	0.4
	HTC 200	0.2	1.6	0.1	0.2	0.6	0.2	95.3	0.3	1.5	0.3
	HTC 230	0.2	1.4	0.1	0.1	0.5	0.2	95.9	0.1	1.8	0.3
	HTC 260	0.2	0.7	0.2	Trace	0.4	0.4	97.3	0.4	1.2	Trace

3.6. *Ash analysis of HTC biochar*

Table 5 shows the elemental percentage in the ash after complete oxidation, but they are only found as an oxide. In ash, the elements Si, Na, Mg, K, S, Ca, P, Al, and Fe are found in the forms of SiO_2, Na_2O, MgO, K_2O, SO_3, CaO, P_2O_5, Al_2O_3, and Fe_2O_3 [14]. Si content dominates in all the HTC biochar ashes studied, with 39–85% of the ash from untreated biomass being Si. The concentration of Si in ash increases with HTC reaction temperature. Up to an 84% decrease in K, and a 46% decrease in Ca is observed for HTC biochar ash. However, Fe, P, S, and Al show an increasing trend up to a HTC reaction temperature of 230 °C for all biochar ash. Comparing HTC at 260 °C to HTC at 230 °C, P decreases for corn stover and miscanthus and remains similar for Fe, S, and Al for all biomass types studied. These trends of the inorganics are consistent with the ICP-AES analysis, so, it can be implied that the inorganics are being inert during ashing at 575 °C.

Several indices of ash and fouling were defined in Table 1. Each index is evaluated for each biomass and each HTC biochar, based on the elemental analyses provided in Tables 3 and 5. Table 6 shows the evaluations of slagging (I_s), fouling (I_F), alkali (I_A), and ratio-slag (I_v) indices, Cl content, and their limits for coal. Slagging and fouling indices of raw biomass reported here are very similar to those reported elsewhere [14,17].

There are two different slagging indices are presented in Table 6. I_s is calculated without considering P concentration, while $I_s + P$ with P concentration in ash. HTC treatment shows the reduction of slagging tendency for every biomass except corn stover. An intermediate tendency of slagging for raw, HTC 230, and HTC 260 are found for corn stover, while, HTC 200 has the higher tendency. Fouling index is also calculated with and without P. If we do not consider P, the fouling tendency improved in HTC 260 for all biochar compared to raw biomass. Fouling tendency is found improved for only corn stover and rice hull with the consideration of P. With respect to ratio slug viscosity (I_V) only raw corn stover shows a medium tendency of slagging, but it is low for other raw biomass and every HTC biochar. Cl is found high in raw and HTC 200 switch grass, is low otherwise in every HTC biochar. In term of alkali index (I_A) only raw corn

Table 6 – Slagging and fouling indices for HTC biochar. Definitions are given in Table 1.

Biomass	Condition	I_S	I_F	I_V	$I_S + P$	$I_F + P$	Cl	I_A
Corn Stover	Raw	Medium	High	Medium	High	High	Low	Probable
	HTC 200	High	Medium	Low	Extremely high	Medium	Low	Probable
	HTC 230	Medium	Medium	Low	Medium	Medium	Low	Low
	HTC 260	Medium	Medium	Low	Medium	Medium	Low	Low
Miscanthus	Raw	Low	Medium	Low	Low	Medium	Low	Probable
	HTC 200	Medium	Medium	Low	Medium	Medium	Low	Low
	HTC 230	Low	Medium	Low	Low	Medium	Low	Low
	HTC 260	Low	Low	Low	Low	Medium	Low	Low
Switch grass	Raw	Medium	Medium	Low	Medium	Medium	High	Probable
	HTC 200	Medium	Medium	Low	Medium	Medium	High	Low
	HTC 230	Low	Medium	Low	Low	Medium	Low	Low
	HTC 260	Low	Medium	Low	Low	Medium	Low	Low
Rice hull	Raw	Low	Medium	Low	Low	Medium	Low	Low
	HTC 200	Low	Low	Low	Low	Low	Low	Low
	HTC 230	Low	Low	Low	Low	Low	Low	Low
	HTC 260	Low	Low	Low	Low	Low	Low	Low

stover, miscanthus, switch grass along with HTC 200 corn stover shows a probable tendency of slagging. But with the increase of HTC temperature, the alkali index is found low regardless of every biochar.

4. Conclusions

Hydrothermal carbonization (HTC) is a promising process for upgrading the mass and energy value of biomass. Hemicellulose degrades completely at 200 °C under hydrothermal conditions, while lignin shows little degradation at 200–260 °C. HTC can remove loose dirt as well as structural ash. HTC treatment can remove up to 90% of Ca, S, P, Mg, and K and >50% Fe, and Mn from biomass. HTC 200 shows effective removal of 72–93% of heavy metals for miscanthus, corn stover, and switch grass. A low fouling index, alkali index, and chlorine content is found with HTC treatment at 230 °C for every biomass.

Acknowledgments

The authors gratefully acknowledge support by Department of Energy (Contract Number: DE-AC07-05ID14517, and DE-EE 0000272). The authors acknowledge meaningful conversations with project partners, including Rachel Imerson, Gerold Gresham, and Jaya Shankar Tamaluru from Idaho National Laboratory and Kent Hoekman of the Desert Research Institute. The authors also acknowledge Chris Sladek, research associate, department of geological science and engineering of University of Nevada Reno for his support with analytical instrumentation.

REFERENCES

[1] Perlack RD, Stokes BJ. ORNL/TM-2011/224. U.S. Department of Energy. U.S. billion-ton update: biomass supply for a bioenergy and bioproducts industry. Oak Ridge; TN: Oak Ridge National Laboratory; 2011. p. 227.
[2] Gilbert P, Ryu C, Sharifi V, Swithenbank J. Effect of process parameters on pelletisation of herbaceous crops. Fuel 2008; 88(8):1491–7.
[3] Michel R, Rapagna S, Di Marcello M, Burg P, Matt M, Courson C, et al. Catalytic steam gasification of *Miscanthus X gigantus* in fluidized bed reactor on Olivin based catalyst. Fuel Process Inst 2011;92(6):1169–77.
[4] Sokhansanj S, Fenton J. Cost benefit of biomass supply and pre-processing enterprises in Canada. Biocap; 2006. Canada.
[5] Peterson AA, Vogel F, Lachance RP, Froling M, Antal MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. Energy Environ Sci 2008;1:32–65.
[6] Titirici MM, Antonietti M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. Chem Soc Rev 2010;39:103–16.
[7] Funke A, Ziegler F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuel Bioprod Bior 2010;4(2):160–77.
[8] Kobayashi N, Okada N, Hirakawa A, Sato T, Kobayashi J, Hatano S, et al. Characteristics of solid residues obtained from hot-compressed-water treatment of woody biomass. Ind Eng Chem Res 2010;48(1):373–9.
[9] Lynam JG, Coronella CJ, Yan W, Reza MT, Vasquez VR. Acetic acid and lithium chloride effects on hydrothermal carbonization of lignocellulosic biomass. Bioresour Technol 2011;102(10):6192–9.
[10] Yan W, Acharjee TC, Coronella CJ, Vasquez VR. Thermal pretreatment of lignocellulosic biomass. Environ Prog Sustain Energ 2009;28(3):435–9.
[11] Acharjee TC, Coronella CJ, Vasquez VR. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Bioresour Technol 2011;102(7):4849–54.
[12] Libra JA, Ro KS, Kammann A, Funke A, Berge ND, Neubauer Y, et al. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, process, and applications of wet and dry pyrolysis. Biofuels 2011;2(1):89–124.
[13] Cuiping L, Chuanzhi W, Yanyonjie Haitao H. Chemical elemental characteristics of biomass in China. Biomass Bioenerg 2004;27(2):119–30.
[14] Masia AAT, Buhre BJP, Gupta RP, Wall TF. Characterising ash of biomass and waster. Fuel Process Inst 2007;88(11–12): 1071–81.
[15] Jenkins BM, Baxter L, Miles TRJ, Miles TR. Combustion properties of biomass. Fuel Process Inst 1998;54(1–3):17–46.
[16] Fahmi R, Bridgwater AV, Darvell LI, Jones JM, Yates N, Donnison IS. The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switch grass, and willow. Fuel 2007;86(10–11):1560–9.
[17] Saddawi A, Jones JM, Williams A, Le Coeur C. Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality. Energy Fuels 2012;26(11):6466–74.
[18] Miles TR, Jenkins BM, Baxter L, Miles TRJ, Bryers RW, Oden LL. Boiler deposits from firing biomass fuels. Biomass Bioenerg 1996;10(2–3):125–38.
[19] Pronobis M. Evaluation of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. Biomass Bioenerg 2005;28(4):375–83.
[20] Goering HK, Van Soest PJ. Forage fiber analysis, USDA Agric. Handbook no 379. Washington DC: Agricultural Research Service, USDA; 1970. 1–9.
[21] Chen SF, Mowery RA, Scarlata CJ, Chambliss CK. Compositional analysis of water soluble materials in corn stover. J Agr Food Chem 2007;55(15):5912–8.
[22] Garrote G, Domínguez H, Parajó JC. Hydrothermal processing of lignocellulosic materials. Eu J Wood Prod 1999;53(3): 191–202.
[23] Bandura A, Lvov A. The ionization constant of water over wide range of temperature and density. J Phy Chem Ref Data 2006;35(1):793–800.
[24] Antal MJ, Mok WSL, Richards GN. Mechanism of formation of 5-(Hydroxymethyl)-2-Furaldehyde from D-glucose and sucrose. Carbohydr Res 1990;199(1):91–109.
[25] Keiluweit M, Nico PS, Johnson MG, Kleber M. Dynamic molecular structure of plant biomass derived black carbon (biochar). Environ Sci Technol 2010;44(4):1247–53.
[26] Yan W, Hastings JT, Acharjee TC, Coronella CJ, Vasquez VR. Mass and energy balance of wet torrefaction of lignocellulosic biomass. Energy Fuels 2010;24(9):4738–42.
[27] Fuertes AB, Arberstain MC, Sevilla M, Macia-Agullo JA, Fiol S, Lopez RJ, et al. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. Aust J Soil Res 2010;48(7):618–26.
[28] Reza MT, Lynam JG, Vasquez VR, Coronella CJ. Pelletization of biochar from hydrothermally carbonized wood. Environ Prog Sustain Energ 2012;31(2):225–34.

[29] Zhang B, Huang H, Ramaswamy S. Reaction kinetics of the hydrothermal treatment of lignin. Appl Biochem Biotechnol 2008;147(1–3):119–31.
[30] Hoekman SK, Broch A, Robbins C. Hydrothermal carbonization (HTC) of lignocellulosic biomass. Energy Fuels 2011;25(4):1802–10.
[31] Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Prog Energ Combust Sci 2005;31(2):171–92.
[32] Verevkin SP, Emel'yanenko VN, Stepurko EN, Ralys RV, Zaitsau DH. Biomass-derived platform chemicals: thermodynamic studies on the conversion of 5-hydroxymethylfurfural into bulk intermediates. Ind Eng Chem Res 2009;48(22):10087–93.
[33] Kalapathy U, Proctor A, Shultz J. An improved method for production of silica from rice hull ash. Bioresour Technol 2002;85(3):285–9.
[34] Nordin A. Chemical elemental characteristics of biomass fuels. Biomass Bioenerg 1994;6(5):339–47.
[35] Jung B, Schobert HH. Improved prediction of coal ash slag viscosity by thermodynamic modeling of liquid-phase composition. Energy Fuels 1992;6(4):387–98.
[36] Flood DT. Flurobenzene. Org Synth 1933;13(2):295–7.